B. Electrochem 4(4) April 1988, pp 369-374

ELECTROCHEMICAL OXIDATION OF ETHANOL AT PLATINUM OXIDE COATED TITANIUM ANODE

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[Received: 1987 July; Accepted: 1988 February]

Platinum oxide coated titanium anode was prepared. Electrooxidation of ethanol in 0.5 mol. dm^{-3} sulphuric acid at these electrodes was studied using galvanostatic polarisation, linear sweep voltammetry and chronopotentiometric techniques. Based on the data obtained, a mechanism is proposed for the electrooxidation of ethanol at these electrodes.

Key words: Ethanol oxidation, platinum oxide coated titanium anode, linear sweep voltammetry, chronopotentiometry

INTRODUCTION

The search for new electrode materials resulted in a great success, when the highly promising properties of oxides of noble metals was disclosed [1]. Soon noble metal oxide coated titanium anodes were introduced into chlor- alkali industry. By their extremely satisfactory performance, these electrodes proved to be a spectacular technological advancement. Noble metal oxide coating is usually obtained as a deposit on titanium substrate by thermal decomposition of the corresponding noble metal chloride film [2].

Although noble metal oxide coated titanium electrodes are actually used in processes other than chlorine evolution [3-5], no detailed kinetic studies exist for other reactions. Only very few investigations of organic reactions appear in the literature [6-12]. It was thus felt desirable to investigate in some detail, the electrooxidation of alcohols on noble metal oxide coated titanium electrodes. Electrochemical oxidation of ethanol at ruthenium oxide coated titanium anode has also been studied [13]. In the present paper, the results of the experiments on the electrochemical oxidation of ethanol on platinum oxide coated titanium anode will be described.

EXPERIMENTAL

Electrodes were prepared by depositing a thin layer of platinum oxide on 1 mm thick plain titanium sheets (15 x 1 cm). The substrate was sand blasted, etched in hot hydrochloric acid, washed well with distilled water and dried. 2% solution of chloroplatinic acid (38% metal content) in isopropanol was prepared and the solution was brushed onto the etched substrate in ten sequential coatings. After each coating, the sample was heated in a drying oven at 373K for 5 minutes to evaporate the solvent and then baked in a preheated funace at 723K for 10 minutes in the presence of air. Between each of the coatings the sample was cooled. After the final coating the sample was heated at 773K for one hour and cooled. The electrodes so prepared had an approximate platinum oxide loading of 2μ mole cm^{-2}. Geometric area of the electrode exposed to the solution was reduced to 1 cm^2 on one side by masking the remaining area using an adherent epoxy resin.

A H-type cell with provisions for gas inlet and outlets and luggin capillary in the working electrode compartment was used. A platinum sheet (area 2 cm^2) served as counter electrode, and saturated calomel electrode (SCE) was employed as reference electrode. Nitrogen gas purified through solutions of alkaline pyrogallol and potassium hydroxide was used for deaeration. Ethanol was purified by standard procedures. 0.5 mol dm^{-3} sulphuric acid prepared by diluting 98% sulphuric acid was used as supporting electrolyte throughout. Potentials were measured vs SCE, but reported vs NHE. Currents are indicated based on geometric area. All measurements, except for the experiments of temperature dependence were carried out at 298 + 0.5K.

For galvanostatic polarisation studies, a dc constant current power supply connected to a decade resistance box and a digital multimeter was used to control polarisation currents precisely. Another digital multimeter was used for measuring electrode potentials. Freshly prepared platinum oxide coated titanium anode invariably recorded a rest potential of 0.98 V in 0.5 mol. dm^{-3} sulphuric acid at 298K. So prior to each experiment, the electrode was conditioned by polarising it potentiostatically at 0.98 V in 0.5 mol. dm^{-3} sulphuric acid, until current dropped to less than 5 μA. At each current, anode potentials were recorded after waiting for a constant time of 30 seconds. Since 0.5 mol. dm^{-3} sulphuric acid was used as supporting electrolyte, the anode potentials were not corrected for IR drop. However, care was taken to place the luggin capillary as close as possible to the anode surface.

For chronopotentiometric studies, the procedure followed by several previous workers [14-17] for the electro-oxidation of organic fuels at platinum electrodes was adopted. The anode was galvanostatically polarised in the supporting electrolyte at a current density of 5 $mA.cm^{-2}$ for 30 seconds before each experiment, so as to ensure complete removal of any oxidisable matter adsorbed on the electrode surface. The anode was then conditioned as mentioned earlier and kept in a solution of 0.5 $mol.dm^{-3}$ ethanol in 0.5 mol. dm^{-3} sulphuric acid for 10 minutes to allow equilibrium to attain between adsorbed alcohol on the anode and the alcohol present in the bulk. After that the anode was taken out, washed well with supporting electrolyte and replaced into a cell containing supporting electrolyte alone. A constant current pulse was then applied across this anode and a large surface area platinum electrode to oxidise the adsorbed alcohol and the corresponding potential variation of the test electrode with time was recorded using a storage oscilloscope (Textronic - 7613). The $\mathcal{E}$ - t transient was stored, traced on a transparent sheet, enlarged and transition time was determined using standard procedures [18]. Since ethanol

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adsorbed on the anode surface was oxidised by polarising the same in supporting electrolyte containing no ethanol, there was no problem of more ethanol diffusing to the anode.

Linear sweep voltammetric studies were carried out by potential sweep method at a sweep rate of 50 $mV.s^{-1}$ in the potential range 0.4 to 1.6 V. The potential of the test electrode was controlled by a potentiostat and the potential sweep was applied by a voltage scan generator. Voltammograms were recorded by a X-y-t recorder.

RESULTS AND DISCUSSION

Preparative electrolysis of 0.5 mol.dm^{-3} ethanol solution in 0.5 mol. dm^{-3} sulphuric acid was carried out and products were analysed. Results indicate that at anode potentials upto 0.95 V, acetaldehyde alone was formed; at potentials between 0.95 V and 1.35 V, a mixture of acetaldehyde and acetic acid was formed and at potentials greater than 1.35 V, acetic acid alone was formed.

The rest potential of platinum oxide coated titanium anode is 0.98 V in 0.5 mol. dm^{-3} sulphuric acid at 298K. Addition of ethanol to the system results in an initial sharp drop in the anode potential which reaches in about 10 minutes a steady value in the range 0.37 to 0.27 V with increasing ethanol concentration. Fig. 1 shows the open circuit potential fall of a freshly prepared platinum oxide coated titanium electrode in 0.5 mol. dm^{-3} sulphuric acid solution containing 0.5 mol. dm^{-3} ethanol.

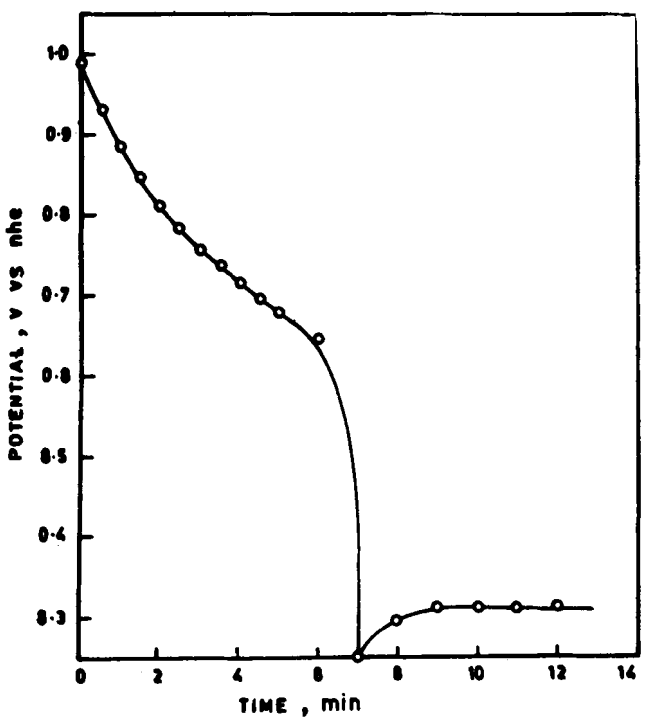

Fig. 1: Open circuit potential fall of a freshly prepared platinum oxide coated titanium anode 0.5 mol. dm^{-3} sulphuric acid on the addition of 0.5 mol. dm^{-3} ethanol at 298K

Similar open circuit potential fall had been observed earlier, when externally anodised platinum electrodes were dipped in solutions containing methanol, formaldehyde and formic acid [19], oxalic acid [20] and ethanol [21]. In all these cases the initial open circuit potential fall leading to a maximum was attributed to the chemical reduction of the platinum oxide by organic species and the subsequent increase of open circuit potential from the minimum to the steady value was ascribed to the adsorption of organic species on the platinum surface. So open circuit potential fall of the platinum oxide coated titanium electrodes in 0.5 mol. dm^{-3} sulphuric acid solutions containing ethanol is due to the following reaction sequence.

$$PtO_X + X\,CH_3CH_2OH \longrightarrow X\,CH_3CHO + Pt + X\,H_2O \quad (1)$$

$$CH_3CH_2OH_{soln.} \underset{}{\overset{Pt}{\rightleftharpoons}} CH_3CH_2OH_{ads} \quad ...(2)$$

It may be rightly assumed that when the platinum oxide coated titanium electrode is dipped in ethanol solution, platinum oxide is reduced to platinum by chemical reaction with ethanol and further electrochemical reactions take place as though, they are taking place on a platinum electrode.

Galvanostatic polarisation studies were carried out in 0.5 mol. dm^{-3} sulphuric acid with different ethanol concentrations (Fig.2).

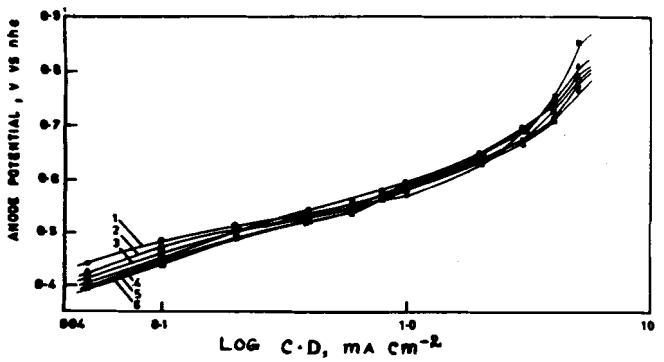

Fig.2: Galvanostatic polarisation curves for the electro-oxidation of ethanol in 0.5 mol. dm^{-3} sulphuric acid on platinum oxide coated titanium anode at different ethanol concentrations (mol. dm^{-3}) at 298K. 1 = 0.1; 2 = 0.2; 3 = 0.4; 4 = 0.6; 5 = 0.8; 6 = 1.0

Tafel slopes were invariably of the order of 2 x 2.303 RT/F in the lower potential region. Rate of ethanol electro-oxidation at constant anodic potential increases with increasing concentration of ethanol (Fig. 3). The order of reaction with respect to bulk concentration of ethanol was determined from the shift of Tafel lines with concentration to be $\left(\frac{\delta \log i}{\partial \log c}\right) \approx 0.2$. Fractional reaction order of 0.5 for formic acid [19], 0.35 for oxalic acid [20] and 0.5 for ethanol [22] had earlier been reported for the oxidation of these

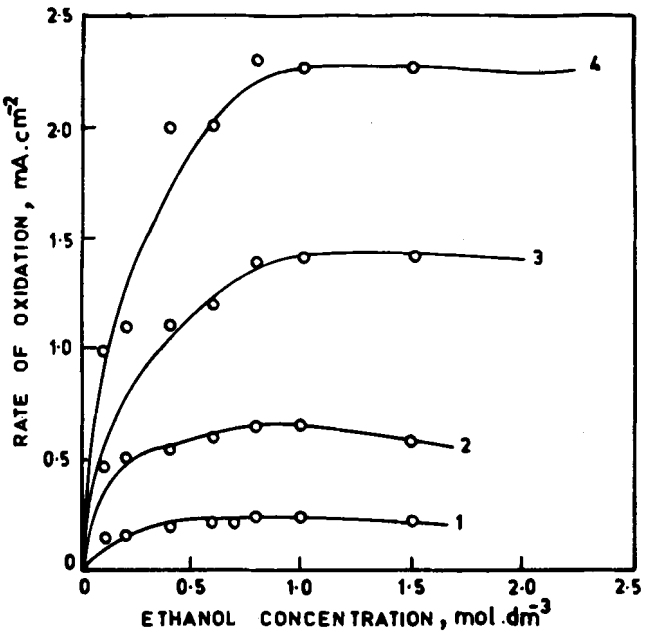

Fig.3: Dependence of reaction rate on ethanol concentration at various potentials for the electro-oxidation of ethanol in 0.5 mol.dm^{-3} sulphuric acid on platinum oxide coated titanium anode at 298K 1 = 0.55V; 2 = 0.60V; 3 = 0.65V; 4 = 0.70V

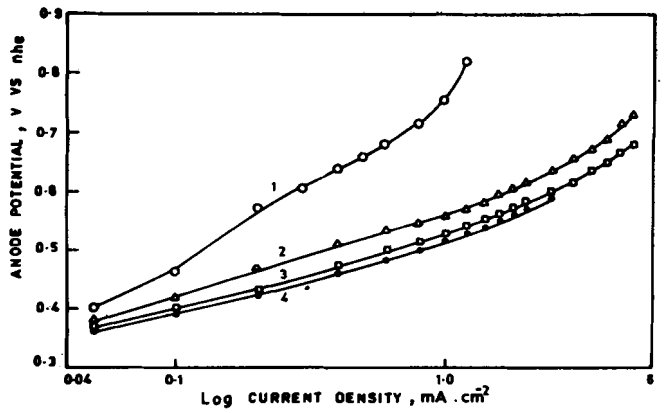

Fig.4: Galvanostatic polarisation curves for the electrooxidation of 0.5 mol. dm^{-3} ethanol in 0.5 mil. dm^{-3} sulphuric acid on platinum oxide coated titanium anode at different temperatures 1 = 290K; 2 = 305K; 3 = 315K; 4 = 325K

compounds at platinum electrodes. Fractional reaction order was inferred to indicate adsorption of the reacting species on inhomogenous surface of platinum electrode. In the present study as platinum oxide coating was obtained on etched titanium sheet whose surface profile had numerous hills and valleys and further platinum surface obtained by in situ reduction of the platinum oxide by ethanol may well be in an inhomogeneous state and hence the fractional reaction order. Exchange current density was found to be 1.6 x 10^{-10} mA.cm^{-2} by extrapolating the linear portion of the Tafel plot to the reversible potential calculated from thermodynamic data. The system was studied at different temperatures and increase of temperature was found to decrease polarisation (Fig 4). Energy of activation for the process was found from the slope of the plot of logarithm current density against inverse temperature, the mean value of which was 10.58 K.cal. mole^{-1} in the lower potential region (Fig. 5).

Chronopotentiometric experiments were conducted at different current densities (i) keeping the ethanol concentration constant after allowing the electrode to adsorb at open circuit potential as well as at a higher potential. Fig. 6 depicts a typical chronopotentiogram for adsorption at open circuit potential. Chronopotentiometric data are shown in Table I. As can be seen from the Table the product '$i\tau^{1/2}$' is not constant and increases continuously as current is increased. This indicates that the process of oxidation of ethanol is not diffusion controlled. The product '$i\tau$' is constant

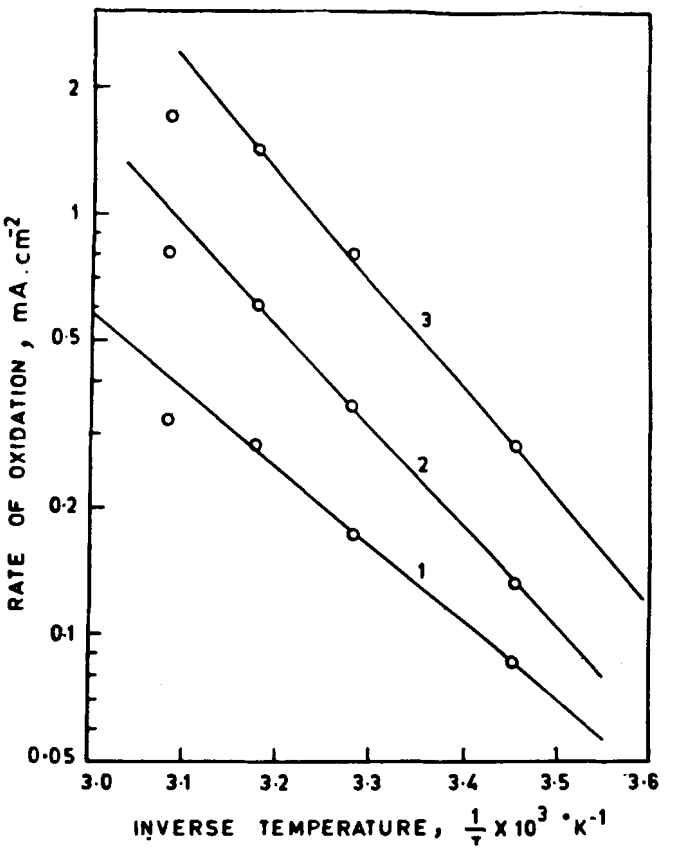

Fig.5: Arrhenius plots for the electrooxidation of 0.5 mol. dm^{-3} ethanol in 0.5 mol. dm^{-3} sulphuric acid on platinum oxide coated titanium anode at various potentials. 1 = 0.50V; 2 = 0.55V; 3 = 0.60V

TABLE-I Chronopotentiometric data

Chronopotentiometric results in 0.5 mol. dm^{-3} ethanol in 0.5 mol. dm^{-3} sulphuric acid solution

Current density (i) ($mA.cm^{-2}$)	Transition time(t) (sec.)	it	$it^{1/2}$
5	9.80	49.0	15.6
10	5.20	52.0	22.8
20	2.60	52.0	32.2
30	1.60	48.0	38.1
40	1.30	52.0	45.6
50	0.98	49.0	49.5
75	0.64	48.0	61.5
100	0.50	50.0	70.7
150	0.33	49.2	85.5
200	0.26	52.0	102.0

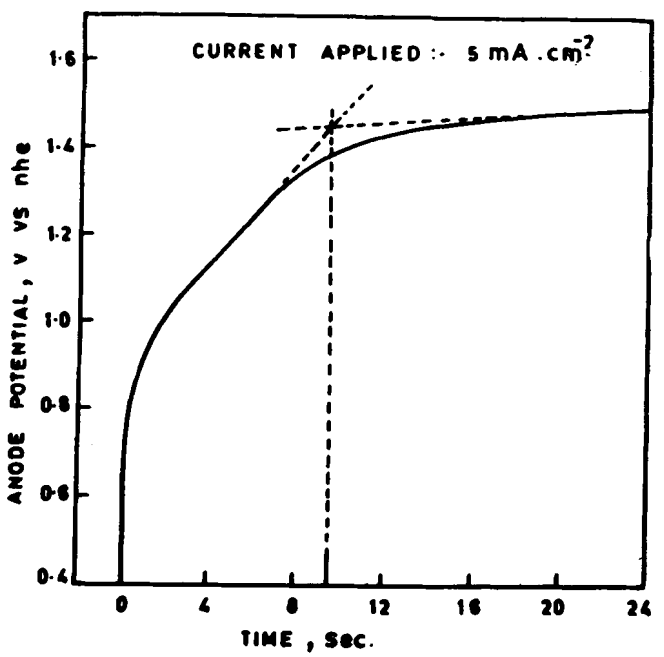

Fig.6: Typical chronopotentiogram for the electrooxidation of 0.5 mol. dm^{-3} ethanol in 0.5 mol. dm^{-3} sulphuric acid on platinum oxide coated titanium anode at 298K

in spite of the increase in current. Further the slope of the plot of $it^{1/2}$ vs i is positive. These observations show that the process is controlled by the oxidation of adsorbed species [23] which is produced by extremely fast rates of adsorption and desorption of the organic species so that equilibrium is maintained between species in the bulk and the species on the electrode surface [24].

Fig. 7 represents the voltammograms obtained in pure sulphuric acid and sulphuric acid solutions of ethanol and acetaldehyde.

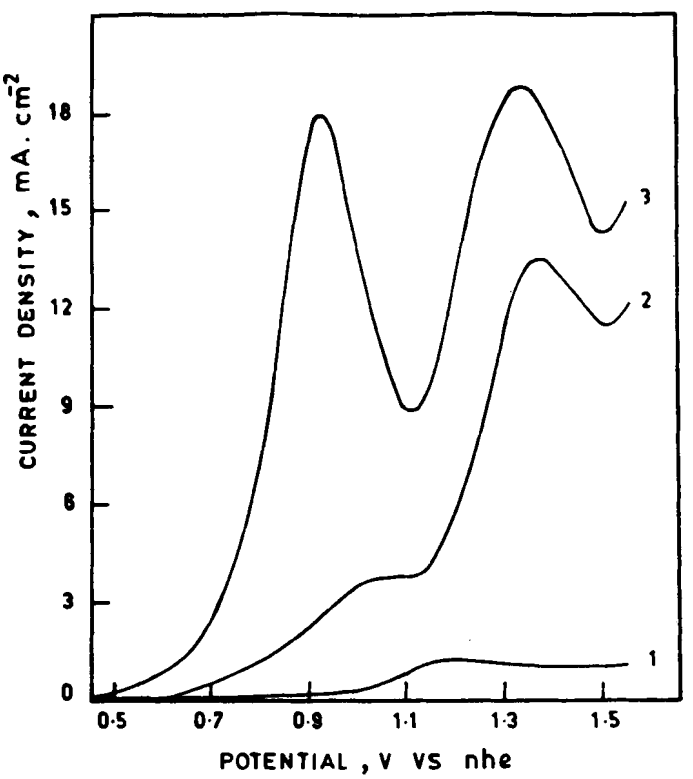

Fig. 7: Linear sweep voltammograms of oxidation of ethanol and acetaldehyde in 0.5 mol. dm^{-3} sulphuric acid on platinum oxide coated titanium anode at 298K sweep rate 50 mV. s^{-1}; 1 = 0.5 M H_2SO_4; 2 = 0.5 M H_2SO_4 + 1.0 M CH_3CHO; 3 = 0.5 M H_2SO_4 + 1.0 M CH_3CH_2OH

In the voltammogram of ethanol, there are two clearly expressed maxima one at 0.90 V and the other at 1.30 V separated by a deep minimum. The corresponding voltammogram of acetaldehyde is characterised with only one well shaped peak at 1.35 V and a prewave at 0.95 to 1.15 V. In voltammogram of H_2SO_4, a plateau appears at about 1.05 V. Exactly similar type of voltammograms were obtained for the electrooxidation of ethanol on smooth platinum [25,26] and on platinised platinum [27]. However peak currents were one order of magnitude higher than those obtained earlier, which may be due to the well accepted higher surface area of thermally prepared noble metal oxide electrodes. The first peak at 0.90 V which was observed only for the system when the electrode was covered with ethanol, corresponds to the oxidation of adsorbed ethanol to acetaldehyde and the second peak at about 1.35 V observed for both ethanol and acetaldehyde corresponds to the oxidation of adsorbed acetaldehyde to acetic acid.

When the potential is increased from open circuit potential, oxidation of adsorbed ethanol takes place. The first step in this oxidation process is the widely accepted dissociative chemisorption of ethanol on platinum leading to the formation of dehydrogenated ethanol radical [25-30]. This radical is present on the platinum electrode at potentials below the E_p of the first peak. However, two different pathways can be suggested for the actual oxidation to acetaldehyde; direct electro-oxidation of the radical or chemical oxidation by adsorbed hydroxyl radical (OH_{ads}). OH_{ads} is produced by low potential oxidation of water [31].

$$H_2O \underset{}{\overset{Pt}{\rightleftharpoons}} OH_{ads} + H^+ + e$$

$$\text{or } Pt + H_2O \rightleftharpoons Pt\text{-}OH + H^+ + e \quad \ldots(3)$$

This reaction takes place on the platinum electrode in the potential range of 0.72 to 0.90 V. Above 0.90 V this reversibly adsorbed OH species undergoes transition to a more stable less reversible form by a place exchange process [31].

$$Pt\text{-}OH \longrightarrow OHPt \quad \ldots(4)$$

It is interesting to note that the onset of the first peak is just below 0.72 V, the potential at which 'Pt-OH' begins to form and that the E_p of the first wave at 0.90 V corresponds closely to the potential at which the transition of 'Pt-OH' to '$OHPt$' starts to occur. So, there is a strong indication that the product acetaldehyde is formed by a chemical reaction between the chemisorbed CH_3CHOH radical and reversibly formed Pt-OH. The first peak in the voltammogram of ethanol would then be due to the electrochemical formation of these surface radicals. This mechanism could be written as

$$CH_3CH_2OH_{soln} \overset{Pt}{\rightleftharpoons} CH_3CH_2OH_{ads} \quad \ldots(5)$$

$$CH_3CH_2OH_{ads} + Pt \longrightarrow CH_3\underset{\underset{Pt}{|}}{CHOH} + H^+ + e \quad \ldots(6)$$

$$\underset{\underset{Pt}{|}}{CH_3CHOH} + PtOH \longrightarrow CH_3CHO + Pt + H_2O \quad \ldots(7)$$

(from eq.3)

The observed Tafel slope of 120 mV per decade indicates that the first electron transfer i.e. step (6) is rate determining. Since bare platinum surface is regenerated for every molecule of acetaldehyde produced, formation of surface radicals is sustained.

It is likely that the less reversible '$OHPt$' species formed above 0.9 V, would be less reactive towards the chemisorbed organic radical. Therefore, as its concentration increases at the expense of more reversible, 'Pt-OH' species, reaction (5) would be slowed down and a decay in the current would be expected, since bare platinum surface would no longer be regenerated. This decay is exactly what is observed, as the potential is increased beyond E_p of the first peak in the case of ethanol. Thus the decay is explained by a build up of species on the electrode surface which are unreactive towards the chemisorbed radical and may also inhibit the formation of chemisorbed radical agreeing with the suggestions of previous workers [25, 27-30,32].

The prewave at 0.95 - 1.15 V in the voltammogram of acetaldehyde is due to the formation of chemisorbed intermediate by dissociative dehydrogenation. Potential arrest is observed, when its formation is hampered by increased surface coverage by oxygen [25].

The occurrence of second peak for ethanol at about 1.35 V indicates that the acetaldehyde present on the surface of the electrode undergoes further oxidation. The voltammograms for both ethanol and acetaldehyde show the second peak at the same potential region indicating that the species undergoing oxidation is the same in both cases. As these peaks appear in the potential region where an oxide layer exists on the platinum electrode, it seems reasonable to assume that the oxide is involved in some manner. The peak in the potential range 1.25V - 1.45 V could be explained by the simultaneously occurring processes of electro-oxidation of the '$OHPt$' species on the electrode surface to 'Pt-O' and subsequent electrochemical reaction between 'Pt-O' and acetaldehyde leading to the formation of acetic acid. The present experimental results do not allow us to determine the relative share of each of these processes involved in the overall anodic reaction.

$$CH_3CHO_{soln} \rightleftharpoons CH_3\,CHO_{ads} \quad \ldots(8)$$

$$OHPt \longrightarrow Pt\text{-}O + H^+ e \quad \ldots(9)$$

$$Pt\text{-}O + CH_3CHO_{ads} + H_2O \longrightarrow$$

$$CH_3COOH + OHPt + H^+ + e \quad \ldots(10)$$

The shift of potential in the anodic direction brings about an increase in the rate of both the electrochemical reactions (9) and (10). As oxide coverage of the surface increases a transition of the surface oxide from the reversible 'Pt-O' form to the irreversible 'OPT' form occurs at about 1.40 V [33,34]. The appearance of the maximum and the subsequent current decay can be explained by the fact that the electrochemical reaction (10) ceases to occur upon the formation of irreversible platinum oxide 'OPt'.

Based on these studies the following mechanism is proposed for the process of electrooxidation of ethanol on platinum oxide coated titanium electrodes.

At open circuit potential: Equations (1) and (2) are applicable.

At anode potentials upto 0.9 V: Reactions corresponding to equations (3), (6) and (7) take place.

Between anode potentials 0.9 to 1.1 V: Reaction as per equation (4) occurs.

Between anode potentials 1.1 to 1.35 V: Reactions proceed according to equations (8), (9) and (10).

Above anode potential 1.35 V

$$Pt\text{-}O \dashrightarrow OPt \quad \ldots(11)$$

Results of the preparative electrolysis studies and the observations of earlier workers [35] that acetaldehyde alone was formed

upto 0.65 V, at more highly anodic potentials a mixture of both acetic acid and acetaldehyde was formed and at potentials greater than 1.9 V, pure acetic acid was formed also support the oxidation scheme, mentioned above.

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